Kinetic evaluations and SADT determination for organic peroxides

Christian Pasturenzi* and Lucia Gigante

Innovhub SSI - Business Area Combustibili, via Galilei, 1 - 20097 San Donato Milanese (MI), Italy

* christian.pasturenzi@mi.camcom.it

Chemical industry often requires the use of very reactive compounds as well as toxic and flammable substances. Among them there are organic peroxides, which are widely used because of their high reactivity; they are used in several reactions, for instance in polymerization. Due to their high reactivity, the use of organic peroxides is very dangerous not only during chemical processes but also during storage and transport.
The thermal decomposition of a substance stored in a container is a process that can be considered adiabatic; the heat generation can bring to an exponential increase of temperature, often with release of flammable vapours and toxic products; also explosions can occur. Therefore knowledge of the thermal stability and kinetics of decomposition of these substances is very important in order to define safe conditions for storage and transport.

The ADR (European Agreement concerning the International Carriage of Dangerous Goods by Road) regulates the transport of dangerous goods by road and Manual of Tests and Criteria by the United Nations separates reactive substances in nine categories; among them there are self-reactive substances (class 4.1) and organic peroxides (class 5.2). A very important parameter to define the carriage conditions for these classes is the Self Accelerating Decomposition Temperature (SADT): this parameter defines whether a temperature control is necessary during the transport. SADT is the lowest temperature at which a self-heating of 6 °C or more within 7 days may occur for a certain substance in the commercial packaging used during carriage.
It's important to keep in mind that SADT is not a chemical-physical parameter, but it derives from a combination of a number of factors: room temperature, kinetics of decomposition, size of the container and heat transfer properties both of the substance and the container.
SADT has to be measured for each commercial container used in transport; Manual of Tests and Criteria reports the four official tests for the determination of SADT:

- The United States SADT test (US SADT test) H1
- Adiabatic storage test (AST) H2
- Isothermal storage test (IST) H3
- Heat accumulation storage test (HAST) H4

Official tests are very time consuming and, because of the big amount of sample, potentially dangerous. For these reasons new methods for the SADT calculation were developed; as described by Fisher and Goetz, they are based on calorimetric techniques such as DSC and ARC.

Another approach, called isoconversional method, well described by Roduit et al.[1], finds interesting applications especially for decomposition reactions. Unlike traditional methods, that provide a single pair of Arrhenius parameters, the isoconversional method gives a trend of the activation energy and pre-exponential factor as function of the reaction progress.
In literature there are three options of the isoconversional method, as described by Budrugeac[2]: the Friedman method, the Ozawa-Flynn-Wall method and the Vyazovkin method.

The aim of this study is to test the robustness of the isoconversional method in order to obtain the kinetic behaviour of a pure substance or a mixture. This kinetic will be consequently used to develop

predictive models of the studied chemicals during storage conditions in order to determine the SADT of the studied packaging.

The used methodology, for the determination of SADT, is based on four simple steps:

- Four DSC or C80 tests at different scanning rate were run
- Calculation of the kinetic of the decomposition reaction. The software AKTS thermokinetics was used
- Validation of the kinetic data through an adiabatic ARC test
- SADT calculation using AKTS thermal safety software

SADT was calculated for three peroxides (diterbutylperoxide DTBP, tert-Butylperoxy 2-ethylhexyl carbonate TBPEHC and a commercial mixture of cyclohexanone peroxide) in a 25 liters HDPE container.
The obtained results are in good agreement with literature data:

- DTBP: isoconversional method 92 °C Vs literature 90 °C
- Cyclohexanone peroxide: isoconversional method 62 Vs literature: > 60 °C
- TBPEHC: isoconversional method 74 °C (literature: n.a.)

The SADT calculation used in this work is based on the collection of experimental data (DSC/C80 dynamic tests) and on the usage of isoconversional method for the kinetic parameters determination and validation. These methods are a real alternative to the official ones: the obtained results are in good agreement with literature data; they are less time consuming and cheaper. Moreover the sample amount in calorimetric tests is very small, so the risk, connected with experimentation, is lower.

[1] Roduit B., Folly P., Berger B., Methieu J., Sarbach A., Andres H., Ramin M., Vogelsanger B., Evaluating SADT by advanced kinetic-based simulation approach, Journal of Thermal Analysis and Calorimetry, 93 (2008) 153-161.
[2] Budrugeac P., Differential non-linear isoconversional procedure for evaluating the activation energy of non-isothermal reactions, Journal of Thermal Analysis, 68 (2002) 131-139.